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Stability and Resistance of Nickel-Based Catalysts for Hydrodeoxygenation

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Introduction

Conversion of biomass through flash pyrolysis followed by hydrodeoxygenation (HDO) has been identified as a prospective path to engine-fuels usable in the current infrastructure [1]. A challenge in HDO, and the scope of the present work, is to obtain sufficient lifetime of the catalyst for this reaction. Aspects of carbon deposition and deactivation from impurities have to be considered. Carbon arises because many of the oxy-compounds of the bio-oil are potential carbon precursors due to their high reactivity. Impurities in the bio-oil can be sulphur, alkali, and chlorine, among others, which all constitute a potential risk to the catalyst [1].

Nickel based catalysts have in recent work been identified as prospective catalysts for HDO with high activity [2]. In the current work the stability and resistance of this type of catalyst is investigated.

Experimental

5 wt% Ni/ZrO₂ was prepared through the incipient wetness method from Ni(NO₃)₂ on a high surface area ZrO₂. Reduction and calcination were done in the setup prior to the experiments at 500 °C with 250 Nml/min H₂ and N₂ for 2 hours. 2.5 g of catalyst diluted in 250 µm glass beads was used in the experiments. All experiments were performed in a new high pressure continuous flow reactor setup with on-line GC-TCD analysis at 250 °C, 100 bar, a gas flow of 400 Nml/min H₂ and 100 Nml/min N₂ and a liquid flow of 0.2 ml/min 10 vol% Guaiacol in 1-octanol; giving a WHSV of 4.1 h⁻¹. Liquid samples were collected at intervals of two hours and analyzed with GC-MS/FID.

Results and discussion

A series of experiments were made where the catalyst was: 1) exposed to sulphur (added as octanethiol corresponding to 0.05 wt% S in the feed); 2) exposed to KCl (predoped to the catalyst); 3) exposed to chlorine (added as chlorooctane

corresponding to 0.05 wt% Cl in the feed); 4) exposed to no poison as a reference case. In all experiments, Ni/ZrO₂ was found to convert the 1-octanol to heptane and initially hydrogenate the guaiacol to 2-methoxy-cyclohexanol followed by deoxygenation to cyclohexane.

The 4 experiments are summarized as degree of deoxygenation (DOD, moles of oxygen removed relative to feed) in Figure 1. The non-poisoned case maintained a constant degree of DOD throughout a period of more than 100 h. Contrary; all three types of poisons severely decreased the activity for deoxygenation. Sulfur was the most severe poison, as the activity dropped to zero in a short time frame after this was introduced in the feed. Chlorine caused a reversible deactivation as the activity could be regained by removing chlorine from the feed. KCl was found as a persistent poisoning, giving a constant low DOD through 24 h of operation.

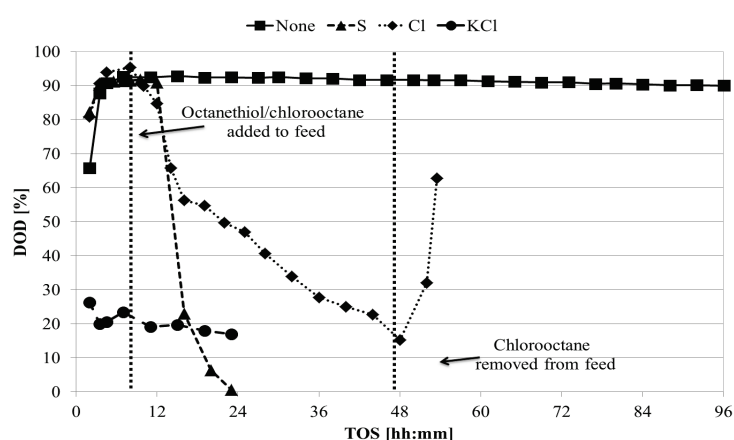


Figure 1. DOD in the three cases with different poisons relative to the case with no poison. Catalyst: 5 wt% Ni/ZrO₂, oil: 10 vol% Guaiacol in 1-octanol, T = 250 °C, P = 100 bar, F_{H₂} = 400 Nml/min, F_{N₂} = 100 Nml/min, F_{oil} = 0.2 ml/min, WHSV = 4.1 h⁻¹

Overall it can be concluded that sulphur, KCl, and chlorine, all will deactivate the catalyst, with the severity of the different phenomena aligning qualitatively as:

$$\text{Sulphur} \gg \text{KCl} \approx \text{Chlorine} \gg \text{Coke}$$

References

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- [2] V.A. Yakovlev, et.al., *Catal. Today*, **2009**, 144, 362

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